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Thermodynamics of Metal Volatility and Speciation in the Molten Salt Oxidation of Organic-Based Radioactive Wastes

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Molten Salt Oxidation (MSO) is a thermal means of completely destroying or mineralizing the organic constituents of mixed and hazardous waste. The flameless catalytic reactions take place at 700 to 950^{o}C in a pool of benign salts, which is usually either sodium carbonate or a eutectic of alkali carbonates. Oxidant air is added with the waste stream into the salt bath, and reactions take place within the salt bath that virtually eliminate the fugitive inventories found in incineration. The organic components of the waste react with oxygen to produce CO_2, N_2, and water. Halogens and heteroatoms such as sulfur are converted to acid gases, which are then “scrubbed” and trapped in the salt in forms such as NaCl and Na_2SO_4. Other incombustible inorganic constituents, heavy metals and radionuclides are held captive in the salt, either as metals or oxides, and if required, these constituents can easily be separated for disposal.

The thermodynamics of this high temperature chemical process are examined, particularly with respect to the behavior of the twelve EPA “problem elements” (Hg/Cd, Pb, Tl/As, Be, Cr, Sb, Ba, Ni, Se, Ag), actinide elements (U, Np, Pu, Am), and potentially volatile fission products such as Cs, Mo, I and Te. Of particular interest are the issues of volatility during primary treatment of radioactive wastes, the final chemical states of elements retained in the salt (relevant to salt reprocessing), and materials compatibility (for containment of the hot salt). Building on direct equilibrium vapor pressure measurements of several important U, Pu and Cr species under typical thermal process conditions, and thermochemical data estimates for other species, our approach has been to use the on-line FACT/EQUILIBRIUM computer code and database to calculate the chemical states of elements of interest at typical temperatures for the MSO process. It will be shown how this information has proved valuable in the design of a pilot-scale MSO process system and flowsheet, and how this analysis has revealed some specific needs for measured thermochemical data.

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